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Secondary α-Deuterium Kinetic Isotope Effects Signifying a Polar Transition State in the Thermolysis of Ring-Substituted *tert*-Butyl Phenylperacetates

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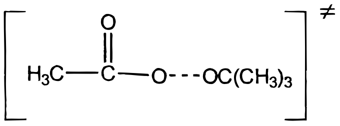
Several ring-substituted *tert*-butyl phenylperacetates ($YC_6H_4CH_2CO_3Bu^t$) and their deuterated versions ($YC_6H_4CD_2CO_3Bu^t$) were prepared (Y: *p*-OCH_3, *p*-CH_3, *p*-H, and *p*-NO_2). Thermolyses at 80 °C in $CDCl_3$ showed excellent first-order kinetics. The rates have been measured as $k_{YH} \times 10^4$ and $k_{YD} \times 10^4$ s^{-1}: 11.9 and 9.20 (*p*-OCH_3), 2.64 and 2.22 (*p*-CH_3), 1.06 and 0.93 (*p*-H), 0.164 and 0.156 (*p*-NO_2). Hammett correlations were derived to yield $\rho_{YH}{}^+ = -1.17$ and $\rho_{YD}{}^+ = -1.12$. However, better Hammett plots were obtained with three points (*p*-OCH_3, *p*-CH_3, and *p*-H) showing $\rho_{YH}{}^+ = -1.35$ and $\rho_{YD}{}^+ = -1.28$. SDKIE was calculated as 1.293 (*p*-OCH_3), 1.189 (*p*-CH_3), 1.140 (*p*-H), and 1.051 (*p*-NO_2), showing substantial substituent effects. Values of k_{YH}/k_{YD} for *p*-NO_2 showed little temperature dependence. Hammett correlations and SDKIE were derived from the same kinetic entity that is the bond cleavage.

Introduction

tert-Butyl peresters[1−3] undergo dual thermal decomposition depending upon the stabilities of radical R• extruded ($RCO_2OBu^t \rightarrow R\bullet + CO_2 + t\text{-}BuO\bullet$). Bartlett et al.[2] showed that two-bond scission exhibits smaller magnitude activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$)[4] than one-bond cleavage. However, this can be conceived by comparing structures of transition state (TS) **1** and **2**. Two-bond homolysis is inevitably accompanied by two partial π-bond formations in **2**. The conjugation of incipient benzyl carbocation introduces a double bond between the benzylic carbon and the phenyl ring. Formation of a CO_2 molecule also yields a C=O bond. Therefore, bond-breakings ($R-CO_2$ and O−O) could be effectively compensated by the formation of double bonds to reduce the enthalpy of activation ($\Delta H^{\ddagger}$). The double bonds then prohibit the rotational motions which act to reduce the entropy of activation ($\Delta S^{\ddagger}$). Surprisingly, the two-bond homolysis[5] also showed less volume of activation (ca. $\Delta V^{\ddagger} = 5$ cm^3/ml) than the one-bond cleavage (ca. $\Delta V^{\ddagger} = 10$ cm^3/mL). The volume of activation[6] is a function of bond rotation and length. Double bonds developed in **2** could restrict the free rotation and contract bond length so as to decrease volume of activation. Therefore, the simultaneous formation of two double bonds can bring about diminutions[7] of activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) when the reactions change from one-bond to two-bond homolysis.



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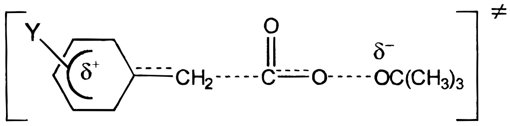

2

Secondary α-deuterium kinetic isotope effects (SDKIE)[8] were reported for **2** with substituent Y being *p*-OCH_3 ($k_H/k_D = 1.07$ at 60.46 °C), *p*-H ($k_H/k_D = 1.13$ at 84.98 °C), and *p*-NO_2 ($k_H/k_D = 1.10$ at 85.1 °C). A k_H/k_D value of 1.13 for *p*-H could be consistent with two-bond homolysis. However, the value for *p*-OCH_3 ($k_H/k_D = 1.06$) appears to hardly reflect electron-donating ability, considering $k_H/k_D = 1.10$ for *p*-NO_2. The studies by substituent/temperature,[2] pressure,[5] and viscosity[9] strongly nominate *p*-OCH_3 as an efficient promoter of two-bond scission.

Results and Discussion

Peresters **3** and their deuterated counterparts **4** were prepared according to the known methods.[2,10] Reactions at 80 °C for 5 half-lives in degassed and sealed Pyrex

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[7] An alternative explanation for variations of activation parameters might employ solvent interactions with the polar TS. Solvent molecules may induce electrostrictions around the polar TS so as to decrease $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. However, reduction of $\Delta H^{\ddagger}$ may be hardly rationalized by solvent effects. Therefore, "double bond formations" could be a more versatile explanation than solvent effects.

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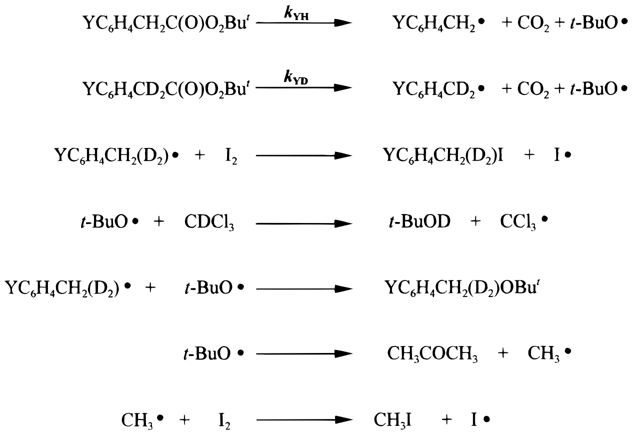
Scheme 1



tubes containing *tert*-butyl phenylperacetate (0.05 M), I_2 (0.2−0.4 M), and acetonitrile (0.02 M, internal standard) in $CDCl_3$ gave rise to formations of benzyl iodide (90.8), *tert*-butyl alcohol (54.3), *tert*-butyl benzyl ether (4.5), methyl iodide (43.3), acetone (43.3) (refer to Scheme 1). The products were identified by comparing the chemical shifts and quantified by integrations of the peaks of appropriate protons of products. The figures in the parenthesis correspond to mol % of products based on the amount of the perester decomposed. The material balance indicates 95.3% conservation of benzyl and 102.1% of *tert*-butoxy.

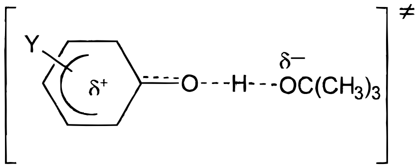
$YC_6H_4CH_2CO_3C(CH_3)_3$ **3**

$YC_6H_4CD_2CO_3C(CH_3)_3$ **4**

(**Y**: *p*-OCH_3, *p*-CH_3, *p*-H, and *p*-NO_2)

The rates (k_{YH} and k_{YD}) were measured by observing periodically the disappearance of **3** and **4** during the decompositions. The magnitude of benzyl protons (δ = 3.6−3.7 ppm) of **3** surviving thermolysis were monitored by FT NMR and used as concentration terms (C_o and C_t) with $\ln(C_o/C_t) = k_{YH}t$. Protons of the *tert*-butyl of **4** (δ = 1.2−1.4 ppm) were excellently resolved by a paramagnetic shift reagent Eu(fod)$_3$[11] from protons of other *tert*-butyl groups, i.e., *tert*-butyl alcohol and benzyl *tert*-butyl ether. Peak area of the *tert*-butyl of **4** was integrated to be utilized as concentrations of **4**. The value of k_{YD} has been derived from $\ln(C_o/C_t) = k_{YD}t$. All of the plots ($\ln(C_o/C_t)$ vs t)[12] showed excellent linearities, with $r \geq 0.997$ in most of the cases, making it possible to assign reliable values of k_{YH} and k_{YD}. The rates and Hammett correlations are tabulated in Table 1. A value for $\rho_{YH}{}^+$ of −1.17 (or −1.35) is consistent with a polar structure of **2** and appears comparable to $\rho^+ = -1.0$ at 80 °C of previous studies.[2] Although **2** involves two-bond homolysis, cleavage of $CO_2-OC(CH_3)_3$ may not be seriously influenced by substituent effects. Therefore, substituents could primarily control the degree of bond-breaking of CH_2-CO_2 only.

Hydrogen abstractions[13] from substituted phenols by the *tert*-butoxy radical revealed $\rho^+ = -0.90$ at 22 °C. *p*-Methoxyphenol ($k = 1.6 \times 10^9$ M^{-1} s^{-1}) reacted faster than phenol ($k = 3.3 \times 10^8$ M^{-1} s^{-1}). However, the former reaction (E_a = 4 kcal mol^{-1}) exhibited higher activation energy than the latter (E_a = 2.8 kcal mol^{-1}). *p*-OCH_3 stabilizes the cationic site, which stimulates an increase in the extent of cleavage of the phenolic O−H in **5**. An enthalpy increase[14] due to such "heterolytic" bond scission could outweigh its reduction caused by the stabilization of the positive charge via conjugations making a double bond. A value of 4 − 2.8 = 1.2 kcal mol^{-1} corresponds to the differential enthalpy of activation ($\Delta\Delta H^{\ddagger}_{Y-H} = \Delta H^{\ddagger}_{Y} - \Delta H^{\ddagger}_{H}$, where $\Delta H^{\ddagger}_{Y}$ is the enthalpy of activation with substituent Y, and $\Delta H^{\ddagger}_{H}$ is the enthalpy of activation with the substituent being hydrogen), which carries a positive sign because *p*-OCH_3 provokes more bond rupture than *p*-H. This enthalpic disadvantage can then be overcome by a much larger differential entropy term ($\Delta\Delta S^{\ddagger}_{Y-H}$ = 6.62 cal K^{-1} mol^{-1}) to achieve rate enhancement. The differential entropy could be expressed as $\Delta\Delta S^{\ddagger}_{Y-H} = \Delta S^{\ddagger}_{Y} - \Delta S^{\ddagger}_{H}$, where entropy terms are defined similarly as with their enthalpic mates. Entropy of activation was calculated from previous data[13] as $\Delta S^{\ddagger}_{Y} = -5.10$ eu for *p*-OCH_3 and $\Delta S^{\ddagger}_{H} = -11.72$ eu for *p*-H. To our surprise, the signs of entropy are negative, which indicates that the decrease[15] in entropy exceeds its increase during the activation process. The positive sign of the differential entropy term ($\Delta\Delta S^{\ddagger}_{Y-H}$ = 6.62 cal K^{-1} mol^{-1}) tells again that *p*-OCH_3 engenders more bond cleavage to create translational entropy[16] larger than that of *p*-H. Our previous radical reactions[17,18] also involved a similar polar TS showing $\rho^+ < 0$ and indicated entropy control of rates. Plots[12] of $\Delta\Delta S^{\ddagger}_{Y-H}$ vs σ^+ gave good linear lines with negative slopes. The negative entity repeatedly suggests that *electron-donating substituents (e.g., p-OCH_3) promote bond-breakings to loosen TS structures.*



5

Structures **2** and **5** share similar features so that comparable substituent effects may act on the bond-breakings. SDKIE[19] could be derived from the promotion of out-of-bending vibrations of methylene when a carbon atom involving bond-cleavage undergoes a hybridization change from sp^3 to sp^2. As previously mentioned, electron-

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[11] Rondeau, R. E.; Sievers, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 1522.

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[14] Formation of an $H-OC(CH_3)_3$ bond in **5** could be relatively immune to substituent effects and may hardly influence the differential term ($\Delta\Delta H^{\ddagger}_{Y-H}$). Substituents primarily control the bond cleavage and subsequent double bond formation, both of which are responsible for formation of enthalpy of activation ($\Delta H^{\ddagger}_{Y}$).

[15] An entropy decrease could be caused by formations of $YC_6H_5=O$ double bond and $H-OC(CH_3)_3$ σ bond in **5**. Formation of the σ bond could significantly progress via hydrogen-bonding and remarkably reduce translational entropy. The double bond prohibits rotations to diminish rotational entropy.

[16] The bond scission creates translational entropy, which could be however partly canceled out by a decrease of rotational entropy due to double bond formation. Translations involve three dimensions, whereas rotations occur with two dimensions. Therefore, an increase of translational entropy may outweigh a decrease of rotational entropy.

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Table 1. Rate Data for Thermolysis of Peresters

$$YC_6H_4CH_2(D_2)CO_3Bu^t \xrightarrow{k_{YH(YD)}} YC_6H_4CH_2(D_2)\bullet + CO_2 + t\text{-}BuO\bullet$$

T, °C	substituent (Y)	$k_{YH} \times 10^4$ s^{-1}	no. of runs[a]	$k_{YD} \times 10^4$ s^{-1}	no. of runs[a]	k_{YH}/k_{YD}
80	p-OCH$_3$[b]	11.9 ± 0.2	6[c]	9.20 ± 0.29	7	1.293
80	p-CH$_3$	2.64 ± 0.02	3	2.22 ± 0.02	4	1.189
80	p-H	1.06 ± 0.01	5[d]	0.93 ± 0.01	3	1.140
80	p-NO$_2$	0.164 ± 0.001	5[e]	0.156 ± 0.002	5	1.051
100	p-NO$_2$	1.44 ± 0.04	3	1.34 ± 0.03	3	1.074
110	p-NO$_2$	3.85 ± 0.02	3	3.62 ± 0.15	3	1.063
120	p-NO$_2$	10.91 ± 0.37	3	10.23 ± 0.23	3	1.066

$\log(k_{YH}/k_{HH}) = \rho_{YH}^{+} \sigma^{+}$
$\rho_{YH}^{+} = -1.17$ ($r = 0.9970$)[f]
$\rho_{YH}^{+} = -1.35$ ($r = 0.9997$)[g]

$\log(k_{YD}/k_{HD}) = \rho_{YD}^{+} \sigma^{+}$
$\rho_{YD}^{+} = -1.12$ ($r = 0.9970$)[f]
$\rho_{YD}^{+} = -1.28$ ($r = 0.9998$)[g]

[a] The figures indicate number of kinetic runs. k_{YH} was measured by monitoring the disappearance of methylene of **3** unless otherwise indicated in footnotes *c*, *d*, and *e*. Rate of diminution of *tert*-butyl of **4** has been used to obtain k_{YD}. [b] Pyridine has been added to stabilize p-CH$_3$OC$_6$H$_4$CH$_2$I ($YC_6H_4CH_2I + C_5H_5N \rightarrow YC_6H_4CH_2NC_5H_5^{+}I^{-}$). The remaining pyridine then interfered with the shift reagent Eu(fod)$_3$ which was therefore treated with methyl iodide ($C_5H_5N + CH_3I \rightarrow C_5H_5NCH_3^{+}\ I^{-}$). [c] Three runs measured the disappearance of *tert*-butyl of **3**. [d] Two runs measured disappearance of *tert*-butyl of **3**. [e] One run measured disappearance of *tert*-butyl of **3**. [f] p-NO$_2$ was included for calculation of correlation coefficients. [g] p-NO$_2$ was excluded for calculation of correlation coefficients.

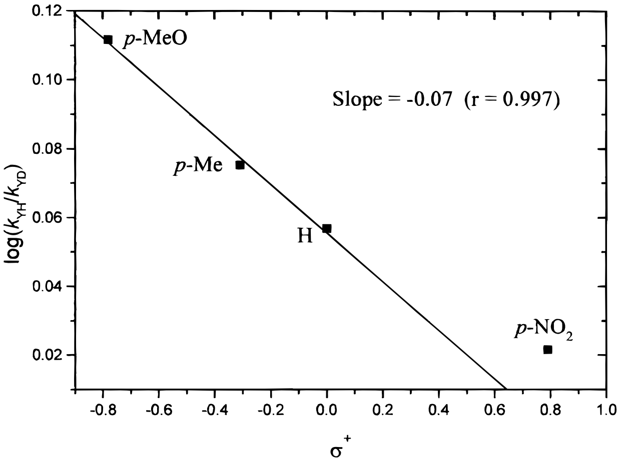

Figure 1.

donating substituents, i.e., p-OCH$_3$, could boost cleavages of CH$_2$−CO$_2$ in **2** and activate bending vibrations of the methylene to give larger values of k_{YH}/k_{YD} (refer to Table 1). A theoretical maximum of SDKIE[20] was assigned as $k_H/k_D = 1.41$. Therefore, changes of k_{YH}/k_{YD} (1.051−1.293) appear substantial to demonstrate strong substituent interactions occurring with the bond rupture. The bond-breaking imparts looseness to the TS structure. An excellent linear relation is observed with three points (Y = p-CH$_3$O, p-CH$_3$, and p-H) in Figure 1. The linearity indicates that the looseness of **2** is systematically controlled by substituents. Looseness of the TS of S$_N$2 reactions[21−23] was also correlated with SDKIE. Substituents[22] engendered quite comparable variations of SDKIE (e.g., $k_H/k_D = 1.039$ for p-NO$_2$ and 1.126 for p-OCH$_3$) when the reactions traversed a symmetrical TS.

Indicated in Table 1 is the fact that electron-donating substituents accelerate the rates of homolysis (k_{YH} and k_{YD}) and intensify the looseness of **2**. Entropy could also be a measure of such looseness. Quite similar behaviors of electron-donating substituents have already been discussed with entropic control of reactions (vide ante and refer to Supporting Information).[13,17,18] p-NO$_2$ shows little variation of k_{YH}/k_{YD} with temperatures, which could be a sign of the entropic dominance. p-NO$_2$ causes the most sluggish rate, which could discourage two-bond homolysis. When p-NO$_2$ is excluded, Hammett plots become improved (Table 1) and Figure 1 maintains a better linearity. These anomalies might mean a changeover of reaction mode. Viscosity studies[9] proposed a dual homolysis mechanism because p-NO$_2$ strongly destabilizes the "cationic moiety" of **2**. Further studies are in progress to probe such delicate changes of bond-breakings.

Conclusions

Although the peresters undergo two-bond homolysis, cleavage of only one bond can be critically influenced by substituent effects. Electron-donating substituents accelerate the rate of homolysis and heighten the extent of bond-breaking. The cleavages bestow looseness upon the TS, which has been figured as values of k_{YH}/k_{YD}. Substituents control SDKIE, i.e., k_{YH}/k_{YD}, which can be an analogue of the differential entropy of activation ($\Delta\Delta S^{\ddagger}_{Y-H}$).

Experimental Section

Materials and Methods. Substituted phenyl acetic acid, *N*,*N*′-carbonyldiimidazole, *tert*-butyl hydroperoxide, and other reagents were purchased from the major suppliers. Liquids were distilled with center-cut collection, and solids were purified according to standard procedures.[24] A Varian Gemini 2000 NMR spectrometer was used for the analysis of the reaction mixtures.

Ring-substituted *tert*-butyl phenylperacetates ($YC_6H_4CH_2CO_3Bu^t$, Y= p-CH$_3$O, p-CH$_3$, and p-H)[10] were prepared by the reactions of the corresponding carboxylic acid, *N*,*N*′-carbonyldiimidazole, and *tert*-butyl hydroperoxide. ***tert*-Butyl p-nitrophenylperacetate (p-NO$_2$C$_6$H$_4$CH$_2$CO$_3$Bu^t)**[2] has been derived from the reactions of p-NO$_2$C$_6$H$_4$CH$_2$COCl and *tert*-butyl hydroperoxide. All the peresters showed IR stretching at 1760−1770 cm^{-1}. ^{1}H NMR data for the peresters (CDCl$_3$ with 0.03% TMS): **p-OCH$_3$** 7.2(d,2H), 6.8(d,2H), 3.79(s,3H), 3.58(s,2H), 1.26(s,9H); **p-CH$_3$** 7.1−7.2(m,4H), 3.60(s,2H), 2.33(s,3H), 1.26(s,9H); **p-H** 7.4−7.2(m,5H), 3.65(s,2H), 1.26(s,9H); **p-NO$_2$** 8.2(d,2H), 7.4(d,2H),3.76(s,2H), 1.28(s,9H). **p-NO$_2$** and

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***p*-OCH$_3$** exhibited melting points of 53−54 and 38−39 °C, respectively.

Ring-substituted *tert*-butyl phenylperacetates-α,α-*d*$_2$ (YC$_6$H$_4$CD$_2$CO$_3$Bu^t, Y= *p*-CH$_3$O, *p*-CH$_3$, *p*-H, and *p*-NO$_2$)[2] were prepared by the reactions of the corresponding acid chloride (YC$_6$H$_4$CD$_2$COCl) and *tert*-butyl hydroperoxide. IR stretching: 1764−1771 cm^{-1}. ^{1}H NMR data (CDCl$_3$ with 0.03% TMS): ***p*-H** 7.4−7.2(m,5H), 1.26(s,9H); ***p*-CH$_3$O** 7.2(d,2H), 6.8-(d,2H), 3.79(s,3H), 1.26(s,9H); ***p*-NO$_2$** 8.2(d,2H), 7.5(d,2H), 1.28-(s,9H); ***p*-CH$_3$** 7.2−7.1(m,4H), 2.33(s,3H), 1.26(s,9H). ***p*-CH$_3$O** and ***p*-NO$_2$** showed melting points of 38−39 and 52−53 °C, respectively.

Ring-Substituted Phenylperacetic Acid-α,α-*d*$_2$ (YC$_6$H$_4$-CD$_2$CO$_2$H, Y= *p*-CH$_3$O, *p*-CH$_3$, and *p*-H). The mixture of phenylacetonitrile (2.48 g, 0.021 mol) and Bu$_4$NBr (0.01 g) was stirred with 1% NaOD in D$_2$O (15 mL) for 2 h at room temperature. More than 99% deutration has been achieved by the repetition of the foregoing procedure. Phenylacetonitrile-α,α-*d*$_2$ (2.40 g, 0.02 mol), NaOD (1.0 g, 0.025 mol), Bu$_4$NBr (0.01 g), and D$_2$O (15 mL) were refluxed for 5 h. After the mixture cooled to 0 °C, concentrated hydrochloric acid (3 mL, 0.03 mol) was added. The precipitate of phenylacetic acid-α,α-*d*$_2$ was filtered off and dissolved in ether (50 mL). The ether solution was separated from the aqueous solution and dried with MgSO$_4$. After evaporation of the ether, the solid was recrystallized from hexane to give 2.04 g (74% yield) of the product. ^{1}H NMR measurements indicated 99% deuteration. ^{1}H NMR data (CDCl$_3$ with 0.03% TMS): ***p*-OCH$_3$** 7.3−7.1(d,2H), 6.9−6.8(d,2H), 3.8(s,3H); ***p*-CH$_3$** 7.2−7.1-(dd,4H), 2.3(s,3H); ***p*-H** 7.26−7.34(m,5H).

***p*-Nitrophenylacetic acid-α,α-*d*$_2$ (*p*-NO$_2$C$_6$H$_4$CD$_2$CO$_2$H)** was prepared by direct nitration of phenylacetic acid-α,α-*d*$_2$. In a 100 mL two-necked round-bottom flask were placed concentrated sulfuric acid (20 mL) and 56% nitric acid (20 mL). The mixture was cooled to 5 °C in an ice bath, and phenylacetic acid-α,α-*d*$_2$ was added slowly at such a rate that the temperature remained at 10 C°. After the addition was completed (ca. 30 min) with removal of the ice bath, the mixture was stirred for 1 h and poured onto crushed ice (100 g). A slightly yellow solid was separated by filtration, washed with ice water, and dissolved in ether (50 mL). The ether solution was separated from the aqueous portion and dried with MgSO$_4$. After evaporation of the ether, the solid was recrystallized from anhydrous ether two times to give 33% yield (3.0 g). *p*-Nitrophenylacetic acid-α,α-*d*$_2$ retained 99% deuteration as measured by ^{1}H NMR. ^{1}H NMR data (CDCl$_3$ with 0.03% TMS): 8.2 (d,2H), 7.5(d,2H). The mp (154−155 °C) agrees with the literature value (154.4−154.8 °C).[2]

Thermal Reactions of Substituted *tert*-Butyl Phenylperacetates. Weighed samples of perester (50 mg), acetonitrile (7 mg, internal standard), and iodine (100−150 mg) were dissolved in CDCl$_3$ (5 mL). The solutions were divided into several Pyrex ampules, which were degassed and sealed by a freeze−pump−thaw method. The ampules (i.d. 4 mm, length 3 cm, 2/3 full) were immersed in a constant-temperature bath for at least 200 s for thermal equilibration. Less than 20 s were required for complete thermal equilibration, which was measured by a Copper−Constantan thermocouple. At various intervals, the tubes were removed from the bath, quenched in ice−water, and opened for NMR analysis.

The integrations of the benzylic peak of a perester at δ = 3.6−3.7 ppm and the peak of acetonitrile (δ = 2.0 ppm) have been made. When integrated values of the perester and acetonitrile are designated as I_P and I_S, respectively, the following equation can be obtained: $I_P/I_S = {}^2/_3 C/C_S$. C and C_S represent the concentrations of the perester and acetonitrile, respectively. Rate constants were then produced by the method of least squares utilizing $\ln(C_o/C_t) = k_{YH}t$. C_o and C_t are concentrations of the perester at time 0 and t, respectively. C_o has been fixed as a concentration of a perester that already underwent homolysis for more than thermal equilibration time. When substituent Y is *p*-CH$_3$, *p*-H, and *p*-NO$_2$, plots of $\ln(C_o/C_t)$ vs t showed excellent linear relations ($r \geq 0.997$). However, the reactions of *p*-methoxy perester did not show simple first-order kinetics. The product analysis suggested that *p*-methoxybenzyl iodide is unstable under the reaction conditions, which could interfere with homolysis of the perester. Pyridine has been added to trap *p*-methoxybenzyl iodide so as to observe first-order kinetics (refer to Supporting Information for plot of $\ln(C_o/C_t)$ vs t).

Thermal Reactions of Substituted *tert*-Butyl Phenylperacetates-α,α-*d*$_2$. Weighed samples of perester (50 mg), CH$_2$Cl$_2$ (25 mg, internal standard), and iodine (300−350 mg) were dissolved in CDCl$_3$ (5 mL). Aliquots (0.7 mL) of the solutions were placed into degassed, sealed Pyrex ampules using a freeze−pump−thaw method. The ampules were immersed in the constant-temperature bath for thermal equilibration. The tubes were then removed periodically from the bath, quenched in ice−water, and opened for NMR analysis. Shift reagent (Eu(fod)$_3$, 0.1−0.2 mg) was added into the reaction mixture for resolution of the proton peaks of various *tert*-butyl groups. The *tert*-butyl of the perester retains a chemical shift at δ = 1.26 ppm. The reaction mixture showed peaks at δ = 1.26 and 5.1 ppm of CH$_2$Cl$_2$, which were integrated to give values of I_P and I_S, respectively. When concentrations of the pereseters and CH$_2$Cl$_2$ are defined as C and C_S, respectively, $I_P/I_S = {}^9/_2 C/C_S$ could be obtained. The rate constants (k_{YD}) were likewise obtained from plots of $\ln(C_o/C_t) = k_{YD}t$ (refer to Supporting Information).

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Supporting Information Available: Plots of $\ln(C_o/C_t) = k_{YH}t$ and $\ln(C_o/C_t) = k_{YD}t$ are provided for the thermal decomposition of YC$_6$H$_4$CH$_2$CO$_3$Bu^t and YC$_6$H$_4$CD$_2$CO$_3$Bu^t at 80 °C, respectively. Plots of $\Delta\Delta S^{\ddagger}_{Y-H}$ vs σ^+ are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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